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A THIOCARBOXYLATE COMPOUND AND A MANUFACTURING METHOD THEREOF

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[There are no amendments to this patent.]

[In this translation, product names are spelled phonetically.]

Specification

1. Title of the invention

A thiocarboxylate compound and a manufacturing method thereof

2. Claims of the invention

(1) A thiocarboxylate compound represented by the following general formula



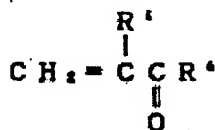
[Wherein, R^1 is a hydrogen atom or a methyl group, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is an alkylene group with 2~5 carbon atoms, and R^5 is a substituted or non-substituted aryl group.]

(2) A method of manufacturing the thiocarboxylate compound described in Claim (1) of the invention consisting of reacting the compound represented by the following general formula



[Wherein, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is a substituted or non-substituted alkylene group with 2~5 carbon atoms, and R^5 is a substituted or non-substituted aryl group.]

and a compound represented by the following general formula



[Wherein, R^1 is a hydrogen atom or methyl group, and R^6 is a hydroxyl group, chlorine atom, or alkoxy group.]

[p. 2]

3. Detailed description of the invention

[Field of industrial application]

The present invention pertains to a polymeric thiocarboxylate compound useful for optical materials and that can be used effectively for paints, inks, adhesives, and photosensitive

resins, etc., and a manufacturing method thereof.

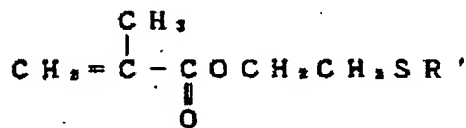
[Prior art]

Many studies have been conducted on synthetic resins to be used in place of inorganic glasses in recent years, but synthetic resins having adequate properties have not been produced. For example, polymers produced by polymerizing a monomer mainly composed of methyl methacrylate or diethylene glycol bis(allyl carbonate) are used for optical resins and lenses, but the refractive index of these materials is low, approximately 1.50.

A variety of resins with high refractive indexes without the above-mentioned problem have been proposed. For example, resins with a high refractive index such as polycarbonates and polysulfones have been proposed. The refractive index of the above-mentioned resins are high, approximately 1.60, but problems such as low light transmittance, insufficient optical uniformity, and discoloration pose problems.

Thus, many crosslinkable monomers for producing resins with high refractive indexes that have an aromatic ring have been proposed in the past. For example, a resin containing a high proportion of halogen atoms where the phenyl group is substituted with halogen atoms such as phenyl methacrylate is proposed in Japanese Kokai [Unexamined] Patent Application No. Sho 61-28901 [1986]. Furthermore, a resin composition with a high refractive index mainly composed of α -naphthylmethacrylate is proposed in Japanese Kokai [Unexamined] Patent Application No. Sho 60-197711 [1985], etc. The above-mentioned monomers used for resins having a high refractive index include halogen atoms and condensed aromatic rings; thus, many of them remain solid at ambient temperatures. Thus, the above-mentioned monomers are polymerized after dissolving in a monomer that remains liquid at ambient temperatures.

For the above-mentioned liquid monomers, methacrylates represented by the following general formula



(wherein R¹ is an alkyl group.)

are known. However, the refractive index of the resin produced as a result of polymerization of the above-mentioned monomer is not sufficient; furthermore, as in the case of standard resins, the scratch resistance of the surface is not sufficient; thus, when used for the purpose of optical applications such as lenses, it is necessary to form a hard coat film on the surface. However, the above-mentioned resin is made of a resin containing methacrylate; thus, when methods commonly applied to allyl diglycol carbonate resins, in other words, methods where an organic silicone film is formed after surface treatment with an alkaline solution, the adhesion between the resin and coated film remains inadequate; thus, the resin cannot be used for practical applications.

[Problems to be solved by the invention]

The purpose of the present invention is to produce a monomer that remains a liquid at ambient temperatures and can be used effectively for dissolving the solid monomers used for producing resins with a high refractive index, and having a high refractive index and low dispersibility, as well as high transparency, high impact resistance, high weather resistance, and that are light weight, etc.

[Means to solve the problem]

As a result of much research conducted by the present inventors in an effort to eliminate the above-mentioned existing problems, they discovered that a thiocarboxylate compound having a specific structure is capable of providing the above-mentioned properties and the present invention was accomplished.

In other words, the present invention is a thiocarboxylate compound represented by the following general formula I



[Wherein, R¹ is a hydrogen atom or methyl group, R² and R³ are the same or different and are hydrogen atoms or alkyl groups, R⁴ is an alkylene group with 2~5 carbon atoms, and R⁵ is a substituted or non-substituted aryl group.]

In the above-mentioned general formula [I], R² and R³ are the same or different and are hydrogen atoms or alkyl groups, and from the standpoint of application of the polymer produced upon carrying out the polymerization reaction to form the optical material, it is further desirable when the above-mentioned group is either a hydrogen atom or a methyl group.

In the above-mentioned general formula [I], the number of carbon atoms in the alkylene group indicated by R⁴ is in the range of 2~5. In the case when the number of carbon atoms is 6 or higher, it is not desirable since the heat-resistance of the resin produced after polymerization of the thiocarboxylate compound of the present invention is reduced.

For the above-mentioned alkylene group, for example, a methyl group, ethylene group, trimethylene group, tetramethylene group, pentamethylene group, propylene group, 1,2-dimethylethylene group, etc. can be mentioned. When the refractive index and heat-resistance of the resin produced are taken into consideration, in general, it is desirable when the number of carbon atoms of the alkylene group is in the range of 2~4.

R⁵ in the above-mentioned general formula [I] is either a substituted or non-substituted aryl group. The carbon atoms of the above-mentioned aryl group is not especially limited, and from the standpoint of viscosity of the compound of the present invention and refractive index of the polymer produced upon conducting the reaction, it is desirable when the number of carbon atoms is in the range of 6~10. For example, a phenyl group, tolyl group, xylyl group, naphthyl group, etc. can be mentioned, and a phenyl group is especially desirable.

The substituents of the aryl group shown in the above-mentioned R⁵ is not especially limited, and halogen atoms, alkoxy groups, alkylthio groups, phenyl groups, phenylthio groups, etc. can be mentioned. As typical examples of the above-mentioned substituted aryl groups, halogenoaryl groups such as chlorophenyl groups, bromophenyl groups, dichlorophenyl groups, dibromophenyl groups, and tribromophenyl groups, methylthiophenyl groups, di(methylthio)phenyl groups, phenylthiophenyl groups, biphenyl groups, etc. can be mentioned.

In this case, the identification of the thiocarboxylate compound shown in general formula [I] above of the present invention was done using the methods described below.

(a) Upon measurement of the infrared absorption spectral (IR), absorption based on CH bond is observed at 3150~2800 cm⁻¹, absorption based on an end double bond is observed at 1650~1620

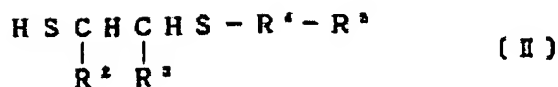
cm^{-1} , and furthermore, the strong absorption of the carbonyl group based on the thioester bond is observed at around $1660\sim 1690\text{ cm}^{-1}$.

(b) The identification of the compound can be easily achieved upon measurement of ^1H -nuclear magnetic resonance spectral (^1H -NMR). Especially, when R^1 in the general formula [I] is a methyl group, the peak based on the methyl group is observed at around $\delta\ 1.9\text{ ppm}$, and peaks based on vinylidene proton are observed at around $\delta\ 5.7$ and $\delta\ 6.1\text{ ppm}$ at a ratio of 3:1:1.

Furthermore, when R^1 is a hydrogen atom, three peaks of hydrogen unique to acrylate are observed at $\delta\ 5.6\sim 7\text{ ppm}$. Furthermore, in the case of a thioether chain, the peak of pattern according to each bonding state of the hydrogen on the carbon atoms bonded with sulfur atoms is shown at around $\delta\ 2.9\text{ ppm}$. Furthermore, in the case when one or the other of R^2 and R^3 is a methyl group, a doublet is observed at around $\delta\ 1.1\text{ ppm}$. Furthermore, the peak based on the aryl group is recognized at $\delta\ 7\sim 8.5\text{ ppm}$, and the peak based on the alkylene group is observed at $\delta\ 1\sim 4\text{ ppm}$. When other hydrogen atoms exist, a spectral pattern based on the bonding state is observed. Identification of the compound can be easily achieved based on the above information.

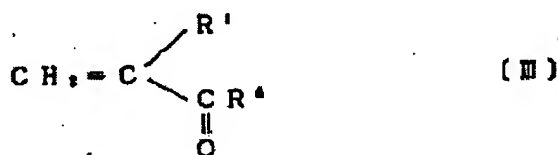
(c) The percentage by weight of oxygen can be calculated when the percentage by weight for carbon, hydrogen, and sulfur are each obtained by means of elemental analysis and the sum of the percentages by weight of each element observed is deducted from 100, and the composition formula for the compound may thereby be determined.

The thiocarboxylate compound shown in general formula [I] may be produced using any method, but, in general, the method explained below is used, and in general, the method wherein the reaction is carried out for a compound represented by the following general formula [II]



[Wherein, R^2 and R^3 are the same or different and are hydrogen atoms or alkyl groups, R^4 is a substituted or non-substituted alkyl group, or a substituted or non-substituted alkylene group with 2~5 carbon atoms, and R^5 is a substituted or non-substituted aryl group.]

and a compound represented by the following general formula [III]



[Wherein, R^1 is a hydrogen atom or methyl group, and R^6 is a hydroxyl group, chlorine atom, or alkoxy group].

[p. 4]

(a) Method where a carboxylic acid is used

It is possible to produce the thiocarboxylate compound shown in general formula [I] when a dehydration condensation reaction is carried out in the presence of an acid catalyst for the compound shown in general formula [II] and a carboxylic acid where R^6 in the compound shown in general formula [III] is a hydroxyl group. The charged molar ratio of both raw materials is determined accordingly, and in general, an excess is used for one or the other compound. For the acid used as the catalyst in the above-mentioned reaction, mineral acids such as hydrochloric acid and sulfuric acid, aromatic sulfonic acids, and Lewis acids such as fluoroboroethylates can be mentioned.

Formation of byproduct water occurs in the above reaction, but the reaction is an equilibrium reaction, thus, refluxing is performed for the solvent with a Dean-Stark moisture separator or a dehydrating agent such as anhydrous sodium sulfate and a molecular sieve are poured into a Soxhlet extractor, or a dehydrating agent such as N,N-dicyclohexylbarbodiimide is added to the reaction system to remove water from the system. For the solvent used in this case, an aromatic hydrocarbon such as benzene or toluene, or an aliphatic hydrocarbon halide such as chloroform or dichloromethane can be mentioned.

The reaction temperature varies depending on the type of solvent used, but, in general, a temperature in the range of 0EC to 120EC is desirable. The reaction time varies depending on the type of raw materials used, but, in general, 30 minutes to 20 hours is suitable, and 1 hour to 6 hours is even more desirable. The method used for isolation and purification of the target material, namely, the compound shown in general formula [I] above, from the reaction system is not especially limited, and known methods can be used in this case as well.

(b) A method whereby a carboxylic acid chloride is used

It is possible to produce the thiocarboxylate compound shown in general formula [I] when a dehydrochlorination treatment is carried out for the compound shown in general formula [II] and a carboxylic acid chloride where R⁶ is a chlorine atom in the compound shown in general formula [III] in the presence of a base. In general, the molar ratio of the both raw materials charged is selected to be in the range of (compound shown in general formula [II])/(compound shown in general formula [III]) = 0.8~1.5, and it is desirable when an equivalence is used.

Byproduct hydrogen chloride is produced in the above-mentioned reaction. In general, it is desirable when a base is included in the reaction system as a hydrogen chloride scavenger, or

an inert gas such as nitrogen gas is supplied to the reaction system so as to eliminate the above-mentioned hydrogen chloride from the reaction system.

The base used for the above-mentioned hydrogen chloride scavenger is not especially limited, and known bases can be used. As bases commonly used, trialkylamines such as trimethylamine, triethylamine, and tripropylamine, pyridine, tetramethyl urea, sodium hydroxide, sodium carbonate, etc. can be mentioned. It is desirable when at least 1 mole of base is used for 1 mole of carbonic acid chloride.

In general, it is desirable when an organic solvent is used for the above-mentioned reaction. For examples of solvents that can be used effectively in this case, aliphatic or aromatic hydrocarbons, and hydrocarbon halides such as benzene, toluene, xylene, hexane, heptane, petroleum ether, chloroform, methylene chloride, and ethylene chloride, ethers such as diethyl ether, dioxane, and tetrahydrofuran, N,N-dialkylamides such as N,N- dimethylformamide, and N,N-diethylformamide, etc. can be mentioned.

The temperature used for the above reaction can be selected over a wide range, but, in general, a temperature in the range of -20EC to 100EC, preferably, 0EC to 50EC can be used effectively. The reaction time varies depending on the type of raw material used, and in general, 5 minutes to 24 hours is sufficient, and 10 minutes to 4 hours is even more desirable. It is especially desirable when stirring is provided during the course of the reaction.

The method used for separation and purification of the target material, namely, the compound shown in general formula [I] above, from the reaction system is not especially limited, and a known method may be used in this case as well.

[p. 5]

(c) Method where carboxylate is used

It is possible to produce the thiocarboxylate compound shown in general formula [I] when a transesterification reaction is carried out for the compound shown in general formula [II] and a carboxylate where R^6 in the compound shown in general formula [III] is an alkoxy group. It is desirable when an acid or a base is used as a catalyst in the above reaction. For examples of acids that can be used effectively as a catalyst, sulfuric acid, hydrochloric acid, p-toluene sulfonate, etc. can be mentioned, and for the base, inorganic bases such as sodium hydroxide, potassium hydroxide, sodium carbonate, and sodium hydrogen carbonate, alkoxide such as sodium methoxide and potassium-t-butoxide, etc. can be mentioned.

An alcohol (R^6H) is produced in the above reaction. The above reaction is an equilibrium reaction; thus, it is desirable to remove the alcohol from the system by means of standard distillation or azeotropic distillation. Thus, it is desirable when a material with R^6 containing an alkoxy group with 1~5 carbon atoms, preferably 1~3 carbon atoms, is used as the raw material carboxylate in general formula [III].

In general, the above-mentioned reaction is carried out without a solvent, but when the raw material is a solid, it is desirable when a solvent having a higher boiling point than that of the byproduct alcohol is used.

As examples of solvents that can be used effectively in this case, aromatic hydrocarbons, and halogen-substituted aromatic hydrocarbon halides such as benzene, toluene, xylene, chlorobenzene, and dichlorobenzene, N,N-dialkylamides such as N,N-dimethylformamide, and N,N-diethylformamide, dimethylsulfoxide, etc. can be mentioned.

The temperature used for the above-mentioned reaction varies depending on the type of

byproduct alcohol, and in general, a temperature whereby the byproduct alcohol undergoes distillation is desirable. The reaction time varies depending on the type of raw material used, and in general, 30 minutes to 24 hours is sufficient, and 2 hours to 8 hours is especially desirable. It is especially desirable when stirring is provided during the course of the reaction.

The method used for isolation and purification of the target material, namely, the compound shown in general formula [I], from the reaction system is not especially limited, and known methods may be used in this case as well.

The thiocarboxylate compound shown in general formula [I] above of the present invention is a liquid monomer having a high refractive index and a polymer having low dispersibility, high transparency, low specific weight, and high impact resistance can be produced. It is possible to carry out a polymerization reaction for the above-mentioned compound by itself, but it is desirable when a copolymerization reaction is carried out with other copolymerizable monomers. The copolymerizable monomer used with the thiocarboxylate compound is selected depending on the purpose and is not especially limited. The thiocarboxylate compound of the present invention is a liquid, thus, the monomer used in this case can be a solid material. For examples of copolymerizable monomers, unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic anhydride, and fumaric acid, acrylate and methacrylate compounds such as methyl acrylate, methyl methacrylate, benzyl methacrylate, phenyl methacrylate, 2-hydroxy ethyl methacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, ethylene glycol bisglycidyl methacrylate, bisphenol A dimethacrylate, 2,2,6,6-tetrabromobisphenol A dimethacrylate, 2,2-bis(4-methacryloyloxy ethoxy phenyl) propane, 2,2-bis(3,5-dibromo-4-methacryloyloxy ethoxy phenyl) propane and

trifluoro methyl methacrylate, thioacrylate and thiomethacrylate compounds such as methyl thiomethacrylate, benzyl thiomethacrylate, phenyl thiomethacrylate, and benzyl thioacrylate, fumarate such as monomethyl fumarate, diethyl fumarate, and diphenyl fumarate, allyl compounds such as diallyl phthalate, diallyl terephthalate, diallyl isophthalate, diallyl tartarate, epoxy diallylsuccinate, diallylmaleate, allyl cinnamate, allyl isocyanate, diallyl hexaphthalate, diallyl carbonate, and allyl diglycol carbonate, aromatic vinyl compounds such as styrene, chlorostyrene, methyl styrene, vinyl naphthalene, isopropenyl naphthalene, bromo styrene, and dibromo styrene, etc. can be mentioned. One or a mixture of two or more different types of the above-mentioned monomers can be used in combination.

[p. 6]

The mixing ratio of the above-mentioned copolymerizable monomers and the thiocarboxylate compounds shown in general formula [I] can be selected from a wide range, and in general, it is desirable when 5~500 percentage by weight, preferably, 10~200 parts by weight, of a copolymerizable monomer is used for 100 parts by weight of the thiocarboxylate compound of the present invention.

It should be noted that a resin with a high refractive index produced by homopolymerization for the thiocarboxylate compound of the present invention or copolymerization with a monomer having one polymeric group among the above-mentioned copolymerizable monomers is a thermoplastic resin. Thus, when the resin is used for applications where a special treatment is required, it is desirable when a copolymerization reaction is carried out with a monomer having at least two polymeric groups as a copolymerizable monomer.

The polymerization reaction method used for production of a polymer comprising a monomer composition containing the thiocarboxylate compound shown in general formula [I] of the present invention or other copolymerizable monomers is not especially limited, and standard radical polymerization reaction may be used in this case as well. As for the means used for initiation of the polymerization reaction, use of a radical polymerization initiator such as peroxides and azo compounds, application of ultraviolet, α -rays, β -rays, γ -rays, and combinations of the above-mentioned methods may be mentioned. As an example of a typical polymerization reaction process, an injection polymerization reaction process wherein the above-mentioned monomer or monomer composition containing a radical polymerization initiator is injected into a mold between dies retained by an elastomer gasket or spacer, curing is performed in an air furnace, and subsequently the cured resin is removed.

The type of radical polymerization initiator used is not especially limited, and standard materials can be used, and as typical examples, diacylperoxides such as benzoyl peroxide, p-chlorobenzoyl peroxide, decanoyl peroxide, lauroyl peroxide, and acetyl peroxide, peroxy esters such as t-butyl-peroxy-2-ethyl hexanate, t-butyl-peroxy neodecanoate, cumyl peroxy neodecanoate, and t-butyl peroxy benzoate, percarbonates such as diisopropyl peroxy dicarbonate, di-2-ethyl hexyl peroxy dicarbonate and di-sec-butyl peroxy dicarbonate, azo compounds such as azobisisobutyronitrile can be mentioned. The mixing ratio of the above-mentioned radical polymerization initiator varies depending on the polymerization reaction conditions used, type of initiator used, and the composition with respect to the above-mentioned monomers used, but, in general, an amount in the range of 0.001~10 parts by weight for 100

parts by weight of the total amount of monomer is adequate, and in the range of 0.001~5 parts by weight is especially desirable.

Among the polymerization reaction parameters, temperature has a significant effect on the properties of the resulting resin with a high refractive index. The above-mentioned temperature is influenced by the type and amount of the initiator and type of the monomer used, and in general, it is desirable when two-stage polymerization reaction is used wherein the polymerization reaction is started at a relatively low temperature and the temperature is slowly increased and curing is done at a high temperature after the polymerization reaction. Furthermore, polymerization reaction time varies depending on a variety of factors as in the case of the polymerization reaction time, and an ideal time is determined according to the above-mentioned conditions, and in general, it is desirable when the polymerization reaction is completed within 2 to 40 hours.

Needless to say, a variety of additives, for example, release agents, ultraviolet absorbers, antioxidants, coloring inhibitors, antistatic agents, fluorescent dyes, dyes, pigments stabilizers, etc. can be used at the time of the above-mentioned polymerization reaction.

Furthermore, the thiocarboxylate compound of the present invention has a single polymeric group in the molecule; thus, a pre-polymerization reaction can be performed to produce a prepolymer and molding can be subsequently carried out, or a polymerization reaction can be carried out to form pellets and molding can be done subsequently to produce the desired optical material.

For production of the above-mentioned prepolymer or pellet, standard polymerization reaction processes can be used. Namely, solid polymerization, solution polymerization,

emulsion polymerization, suspension polymerization, sedimentation polymerization, etc. can be used.

[p. 7]

Furthermore, the treatments described below also can be carried out for the resin with a high refractive index produced by the methods mentioned above. In other words, dyeing with a dispersion dye, etc., hard coating with a hardcoat agent mainly comprising a sol such as a silane coupling, and oxides such as silicon, zirconium, antimony and aluminum, or a hardcoat agent mainly comprising an organic polymer, an antireflecting treatment consisting of depositing a thin film of metal oxide such as SiO_2 , TiO_2 or ZrO or coating of a thin film of an organic polymer, antistatic treatment, etc. also can be applied.

[Effect of the invention]

The thiocarboxylate compound of the present invention remains in liquid form at ambient temperatures and the compound can be used effectively as a monomer for dissolving the monomers of resins with a high refractive index that remain solid at ambient temperature. Furthermore, the polymer produced by polymerization of the thiocarboxylate compound of the present invention has a high refractive index, and excellent transparency, weather resistance, and impact resistance can be achieved; furthermore, the refractive index is 1.57 or higher and the dispersibility is low, and excellent transparency and reduced weight can be achieved. Therefore, the resin with a high refractive index made of a homopolymer of the thiocarboxylate compound of the present invention or a copolymer of the above-mentioned compound and a copolymerizable monomer can be used effectively as an organic glass, for example, optical

lenses used for eyeglasses, lenses for optical instruments, as well as for prisms, optical disk bases, optical fibers, etc.

[Application Examples]

In the following, the present invention is explained in further detail with Application Examples, but the present invention is not limited to these Application Examples.

In this case, the identification of the thiocarboxylate compound produced in the present invention was done using the methods described below.

(1) IR spectral analysis

The sample was placed between KBr boards and the measurement was made with the sample in the form of a thin film using the IR-440, a product of Shimazu Co., Ltd.

(2) ^1H -NMR spectral analysis

The sample was diluted with CDCl_3 and measurements were made with tetramethylsilane as the internal standard using a PMX-60S1 (60 MHz), product of Nihon Denshi Co., Ltd.

(3) Elemental analysis

An analysis was made for the carbon and hydrogen by a CHN Corridor, Model MT-2, product of Yanagimogo Co., Ltd., and measurements were made for sulfur using the flask burning method.

(4) Refractive index (n_D^{20})

Measurements were made of the refractive index at a temperature of 20EC with an Abbe Refractometer (Model 3T) product of Atago (Ltd.).

Furthermore, measurements were made of the properties of the resins with high refractive indexes produced in the Application Examples according to the test methods described below.

(1) Refractive index (n_D^{20}), Abbe number (ν)

Measurement of the refractive index and Abbe number was done at a temperature of 20EC with an Abbe Refractometer (Model 3T) product of Atago (Ltd.). For the contact solution, bromonaphthalene was used.

(2) Surface appearance

A visual evaluation was made.

(3) Weather resistance

A sample was positioned in Long-life Xenon Fadometer, (Model FAC-25AX-HC) product of Suga Testing Machines (Ltd.), an exposure was made with xenon rays for 100 hours, and the degree of discoloring of the sample was evaluated visually and those having a degree of discoloring less than that of polystyrene are identified by \pm , those having about the same or higher degree of discoloration are identified by a triangle and those having a higher degree of discoloration are identified by an x.

(4) Impact resistance

A steel ball with a specific weight was dropped onto a sample sheet punched out to form a disc with a thickness of 2 mm and a diameter of 65 mm from a height of 127 cm, and the maximum weight of the steel ball that did not cause breakage in the sample disc was measured. Subsequently, an evaluation was made according to grades A~E shown in Table I.

Table I

Weight of steel ball	Grade
80 g or higher	A
80 g or less but higher than 60 g	B
60 g or less but higher than 40 g	C
40 g or less but higher than 20 g	D
20 g or less	E

[p. 8]

(5) Adhesion of hardcoat film

A thorough cleaning was performed for the sample sheet-like resin with methanol, air drying was further performed, then, the resin was dipped in a 10% sodium hydroxide solution for 10 minutes. Subsequently, a water wash was provided and drying was performed so as to provide a pre-treatment for the sample. Meanwhile, thorough mixing was performed for 20 parts by weight of bis(γ -triethoxy silyl propyl) carbonate, 10 parts by weight of γ -glycidoxy propyl trimethoxy silane, 30 parts by weight of colloidal silica (product of Nissan Chemical Corp., methanol solution), 30 parts by weight of methyl cellosolve, 10 parts by weight of 0.05N hydrochloric acid and 0.25 parts by weight of ammonium perchlorate, and production of a hardcoat solution was carried out. The above-mentioned pre-treated sample was dipped in the above-mentioned hard coat solution produced, a thorough air drying was performed at room temperature, heating was provided for 3 hours at a temperature of 80EC to cure the film.

An evaluation of the coated film produced was done using the test method explained below. 100 squares measuring 1 mm x 1 mm were formed on the surface of the sample with a cutting blade having a sharp tip, a commercial cellophane tape was applied, rapid peeling was performed, then, the peeled state of the film was visually examined and the number of squares

remaining were counted.

In this case, the monomers used in the following Application Examples are identified by the codes explained below. Furthermore, the numbers shown in [] are the refractive index of the homopolymer.

Br₃PMA: 2,4,6-tribromophenyl methacrylate [1.625]

ClSt: Chlorostyrene (mixture of o-member and m-member) [1.610]

VDF: 2-vinyl benzofuran [1.679]

Br₂St: Dibromostyrene [1.657]

BBMEPP: 2,2-bis(3,5-dibromo-4-methacryloyloxy ethoxy phenyl) propane [1.600]

BMEPP: 2,2-bis(4-methacryloyloxy ethoxy phenyl) propane [1.558]

BTM: Benzylthiomethacrylate [1.620]

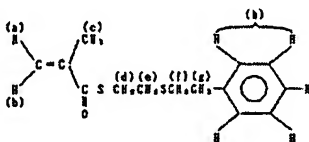
DEGM: Diethylene glycol dimethacrylate [1.508]

St: Styrene [1.590]

Application Example 1

19.9 g (0.10 moles) of 2-phenyl ethyl thioethyl thiol, 7.9 g (0.10 moles) of pyridine and 100 ml of anhydrous chloroform were charged to a throuree-neck flask equipped with a thermometer, stirring device and dropping funnel and cooling was performed to 0EC. Subsequently, 10.5 g (0.10 moles) of methacrylic acid chloride was slowly added dropwise as stirring was performed. At this time, the reaction temperature was maintained at 0~5EC, and further stirring was performed for 1 hour at a temperature of 20EC after the above-mentioned addition was completed. Then, the reaction mixture was poured into water, washing of the organic layer was carried out with a dilute sodium carbonate solution and a further water wash

was performed. Drying of the organic layer was done with anhydrous magnesium chloride and removal of the solvent was performed under a vacuum so as to produce 18.7 g of the target 2-phenyl ethyl thioethyl thiomethacrylate in the form of a colorless transparent liquid. The refractive index of the material produced above was 1.579. The IR chart of the material produced is shown in Fig. 1. As shown in the Fig., absorption based on intense carbonyl group was observed at 1640 cm^{-1} , and absorption based on the end double bond was observed at 1640 cm^{-1} . Furthermore, $^1\text{H-NMR}$ (based on tetramethylsilane in CDCl_3 solvent, ppm) chart is shown in Fig. 2. As a result, three peaks based on the hydrogen of the methyl group (c) were observed at $\delta\ 1.93$ as a doublet of coupling constant 2Hz, eight peaks based on the hydrogens of methylene (d), (e), (f) and (g) were observed at $\delta\ 2.3\sim 3.3$ as a multiplet, a peak based on the hydrogen (a) of vinylidene group was observed at around $\delta\ 5.56$ as a doublet, a peak based on the hydrogen (b) of vinylidene group was observed at around $\delta\ 6.05$ as a doublet, and five peaks based on the hydrogen of phenyl group (h) were observed at around $\delta\ 7.1$ as a multiplet, respectively.



[p. 9]

In this case, values obtained by elemental analysis were C: 63.32% (63.11%), H: 6.99% (6.81%) and S: 23.93% (24.07%) (the theoretical values are shown in ()) and correspond well with the theoretical values.

Application Examples 2~8

Production of thiocarboxylate compounds was performed with the raw materials shown in Table II below as in the case of Application Example 1. Properties of the thiocarboxylate compounds produced are shown in Table II as well.

Table II

	Application Example	Thiocarboxylate compound	Characteristics	Refractive index n _D ²⁰	IR (cm ⁻¹) ν (C=O)	Elemental analysis (%), theoretical values shown in ()		
						C	H	S
	2	$\text{CH}_2 = \text{CHCO}_2\text{C}_2\text{H}_4\text{S}-\text{C}_6\text{H}_5$ 	Colorless, transparent liquid	1.579	1665	63.38 (63.11)	6.60 (6.81)	23.84 (24.07)
	3	$\text{CH}_2 = \text{CClCH}_2\text{COS C}_2\text{H}_4\text{S}-\text{CH}_2\text{CH}(\text{CH}_3)-\text{C}_6\text{H}_5$ 	"	1.582	1670	64.01 (64.24)	7.48 (7.19)	22.59 (22.87)
	4	$\text{CH}_2 = \text{C}(\text{H})\text{COS C}_2\text{H}_4\text{S}-\text{CH}_2\text{CH}(\text{CH}_3)-\text{C}_6\text{H}_5$ 	"	1.581	1665	64.08 (64.24)	7.34 (7.19)	23.03 (22.87)
	5	$\text{CH}_2 = \text{CClCH}_2\text{COS C}_2\text{H}_4\text{SCH}_2\text{CH}_2-\text{C}_6\text{H}_5$ 	"	1.582	1670	64.35 (64.24)	7.47 (7.19)	23.02 (22.87)
	6	$\text{CH}_2 = \text{CH COS C}_2\text{H}_4\text{SCH}_2\text{CH}_2-\text{C}_6\text{H}_3\text{Br}_2$ 	Colorless, transparent, viscous material	1.598	1670	37.98 (38.05)	3.46 (3.42)	15.55 (15.61)
	7	$\text{CH}_2 = \text{CClCH}_2\text{COS C}_2\text{H}_4\text{S}-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{SCH}_2\text{C}_6\text{H}_5$ 	"	1.591	1670	57.84 (57.65)	6.55 (6.45)	30.52 (30.78)
	8	$\text{CH}_2 = \text{CClCH}_2\text{COS C}_2\text{H}_4\text{S}-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$ 	"	1.590	1670	70.37 (70.13)	6.51 (6.47)	18.61 (18.72)

Application Example 9

As a radical polymerization initiator, 1 part by weight of t-butylperoxy-2-ethyl hexanate was added to 100 parts by weight of thiocarbonate compounds produced in the above-mentioned Application Examples 1~8 and thorough mixing was performed. The above-mentioned mixed solution was poured into a die made of a gasket structured of a glass sheet and ethylene-vinyl acetate copolymer and a polymerization reaction was performed. The above-mentioned mixed solution was poured into a die made of a gasket structured of a glass sheet and ethylene-vinyl acetate copolymer and a polymerization reaction was carried out. In this case, the above-mentioned polymerization reaction was performed in an air furnace and the temperature was slowly increased from 30EC to 90EC in 18 hours and the temperature was then retained at 90EC for 2 hours. After the above-mentioned polymerization reaction, the removal of the die was performed from the air furnace, natural cooling was performed, and the polymer was removed from the glass die. Measurement was performed for the properties of polymers produced and the results obtained are shown in Table III.

Comparative Examples 1 and 2

As monomers, methyl methacrylate and 2-methyl thioethyl methacrylate were used and a treatment was performed as in the case of Application Example 9. And the properties of polymers produced are shown in Table III in this case as well.

Table III

No.	Application Example No. of thiocarboxylate compound	Surface appearance	Specific gravity	Refractive index n_D^{20}	Abbe number ν	Weather resistance	Impact resistance	Adhesion of the coated film
1	1	Colorless, transparent	1.21	1.632	34	±	A	100
2	2	"	1.21	1.633	34	±	A	100
3	3	"	1.20	1.627	35	±	A	100
4	4	"	1.18	1.625	35	±	A	100
5	5	"	1.19	1.625	36	±	A	100
6	6	"	1.61	1.644	33	±	A	100
7	7	"	1.23	1.638	34	±	A	100
8	8	"	1.17	1.636	34	±	A	100
Comp Ex 1	$\text{CH}_2=\text{CCH}_3\text{COS-CH}_3$	"	1.20	1.587	35	±	D	100
Comp Ex 2	$\text{CH}_2=\text{CCH}_3\text{COO-CH}_2\text{CH}_2\text{SCH}_3$	"	1.19	1.521	43	±	B	20

Translator's note: Comp Ex = Comparative Example

[p. 11]

Application Example 10

Compositions comprising the thiocarboxylate compounds shown in Table IV below and copolymerizable monomers are used in this case and a treatment was performed as in the case of Application Example 9. And the properties of polymers produced are shown in the following Table IV.

Table IV

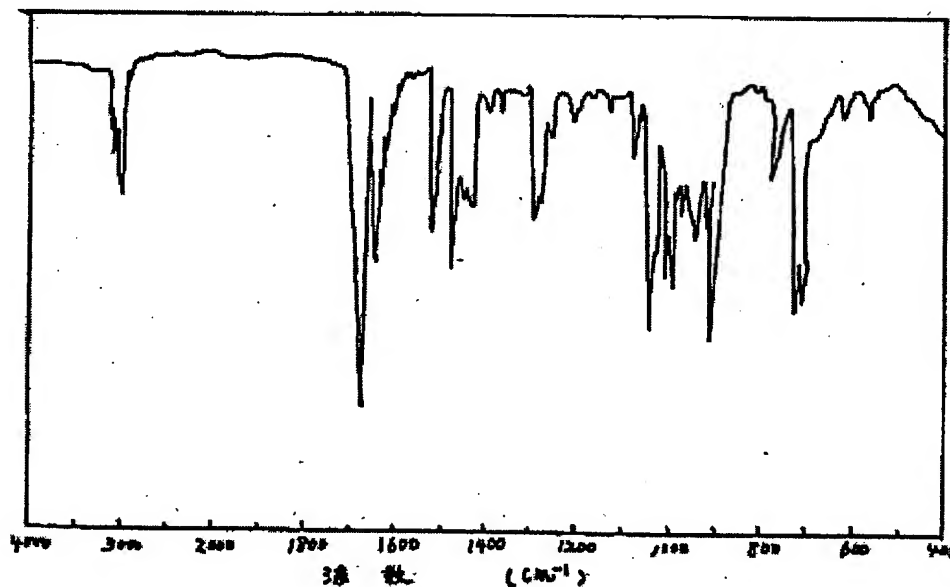
	Monomer composition (parts by weight)				Surface appearance	Specific gravity	Refractive index n_D	Weather resistance
	Application Example No. of thiocarboxylate compound		Copolymerizable monomers					
1	1	(80)	Br ₃ PMA	(20)	Colorless, transparent	1.34	1.631	±
2	"	(60)	"	(40)	"	1.46	1.629	±
3	"	(60)	ClSt	(40)	"	1.22	1.623	±
4	"	(60)	Br ₂ St	(40)	"	1.49	1.642	±
5	"	(60)	VDF	(40)	"	1.21	1.651	±
6	"	(40)	"	(60)	"	1.20	1.660	±
7	"	(80)	BMEPP	(20)	"	1.21	1.617	±
8	"	(60)	BMEPP	(40)	"	1.20	1.619	±
9	"	(50)	BTM	(50)	"	1.21	1.626	±
10	2	(50)	ClSt	(50)	"	1.19	1.622	±
11	"	(50)	BMEPP	(50)	"	1.21	1.596	±
12	4	(50)	ClSt	(50)	"	1.21	1.618	±
13	"	(70)	BMEPP	(30)	"	1.19	1.605	±
14	5	(50)	ClSt	(50)	"	1.21	1.618	±
15	6	(50)	St	(50)	"	1.33	1.617	±
16	7	(70)	BMEPP	(30)	"	1.22	1.615	±
17	8	(80)	"	(20)	"	1.18	1.620	±
18	8	(80)	DEGM	(20)	"	1.15	1.611	±

4. Brief description of figures

Fig. 1 and Fig. 2 are, respectively, the infrared absorption spectrum and the ^1H -nuclear magnetic resonance spectrum of the thiocarboxylate compound produced in Application Example 1.

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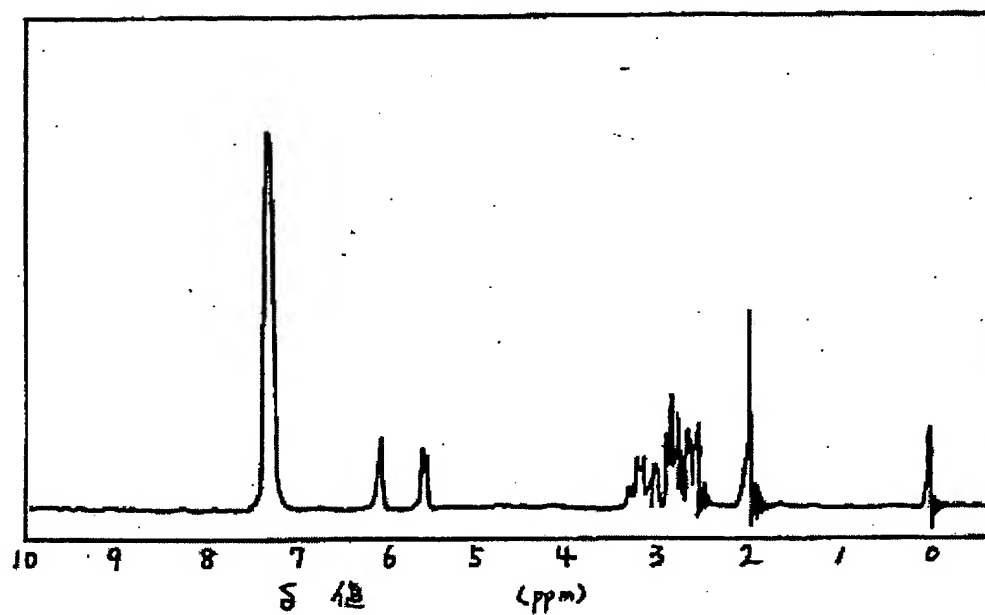
Fig. 1



Horizontal axis: Wavelength (cm^{-1})

[p. 12]

Fig. 2



Horizontal axis: δ value (ppm)

